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## Atomistically Informed Continuum Model of Polymer-Based Nanocomposites

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### ABSTRACT

A model polymeric material filled with spherical nanoparticles is considered in this work. Monte Carlo simulations are performed to determine the polymer chain conformations in the vicinity of the curved interface with the filler. Several discrete models of increasing complexity are considered: the athermal system with excluded volume interactions only, the system in which entropic and energetic interactions take place while the filler is a purely repulsive sphere, and the system in which both filler-polymer and polymer-polymer energetic interactions are accounted for. The total density, chain end density, chain segment preferential orientation and chain size and shape variation with the distance from the filler wall are determined. The structure is graded, with the thickness of the transition region being dependent on the property and scale considered. Hence, the polymer in the vicinity of the filler is represented in the continuum sense by a material with graded properties whose elasticity is determined based on the local structure. Homogenization theory is used to obtain the overall composite moduli. The filler size effect on the composite elasticity is evaluated.

### INTRODUCTION

Polymer-based nanocomposites form a new class of reinforced polymers in which the fillers have at least one dimension less than 100 nm. These materials have macroscopic properties significantly different from those of conventional composites of same filler volume fraction [e.g. 1,2]. For example, the dispersion of only 2% volume fraction of nanoparticles in thermoplastics almost doubles the yield stress and increases the Young's modulus.

The mechanisms responsible for the enhanced properties are not fully understood and controlled. It appears that interesting properties are obtained when the filler size and/or the filler wall-to-wall distance become comparable with the chain radius of gyration. Two principal ideas have been promoted in this connection: the novel properties are either due to chains connecting several fillers (the double network theory), or to the special distribution and density of entanglements in the confined polymer matrix. In all situations, it is generally accepted that the structure of polymeric chains confined between fillers and their binding to the wall are the major elements controlling the properties of the composite.

This work is part of an ongoing effort to relate the polymer structure to the macroscopic nanocomposite properties. We consider a model polymer filled with spherical impenetrable particles. The chain structure in the vicinity of fillers is determined by Monte Carlo simulations. The elasticity of the matrix is determined based on the local structure. The composite is homogenized for its overall elastic properties. We first review the main features of the polymer structure at the wall, then we present the procedure by which the continuum model is calibrated based on the discrete structure, and finally, we discuss the filler size effect on composite moduli.

## Polymer structure in the vicinity of fillers

Lattice Monte Carlo simulations are performed to determine the polymer structure in the vicinity of fillers. A simulation cell containing a single filler is used (with periodic boundary conditions). The polymers are represented by a “pearl-necklace” model. The beads are free to move on a lattice surrounding the filler, the chain connectivity and the excluded volume conditions being enforced at all times. The model and the simulation procedure are described in detail in [3]. The parameters of the model are the chain size ( $N$ ), the filler radius ( $R$ ) and the filler volume fraction. Various types of interactions are considered in separate models: excluded volume only, excluded volume and energetic interaction in bulk polymer, excluded volume and energetic interaction between polymers and the filler. The results reported here are for the system with  $R = 8$ ,  $N = 100$  ( $R_g = 4.7$ ) and filler-to-filler distance  $L = 32$  (wall-to-wall distance of 16, i.e. twice the chain size,  $4R_g$ ). All dimensions are in multiples of the bond length (equal to the unit of length used in the Lennard-Jones potential representing non-bonded interactions).

The total bead number density normalized by the bulk density is shown in Fig. 1a for the case in which no filler-polymer interactions are imposed. The curve labeled “athermal” corresponds to the purely entropic system in which only excluded volume interactions are allowed. This corresponds to the “high temperature” situation in which the entropic component of the free energy dominates. The curve labeled “energetic” corresponds to the system in which cohesive interactions in the bulk polymer are considered. An ample depletion layer forms next to the filler, and effect also observed in lattice MC simulations of structure next to flat interfaces. We note that continuous space discrete models predict strong density oscillations next to the wall due to packing and no depleted layer. The effect seen here is pronounced in the energetic case (low temperatures), while in the athermal system it is absent, the bead density being constant.

An entropic driving force exists for chain end segregation in the interface. The chain end number density is shown in Fig 1a for the energetic system. The end segregation has no effect on the elastic moduli of the matrix. The effect of the various model parameters is discussed in [3].

The chain number density is evaluated based on the position of the chain centers of mass with respect to the wall (Fig. 1b). The volume surrounding the filler is divided in spherical bins (concentric layers) of thickness equal to 2. The data points represent the density in each layer normalized with the bulk chain number density. The chain density is lower at the wall than in the bulk, an effect due to the excluded volume of the filler. The depletion is also driven by the

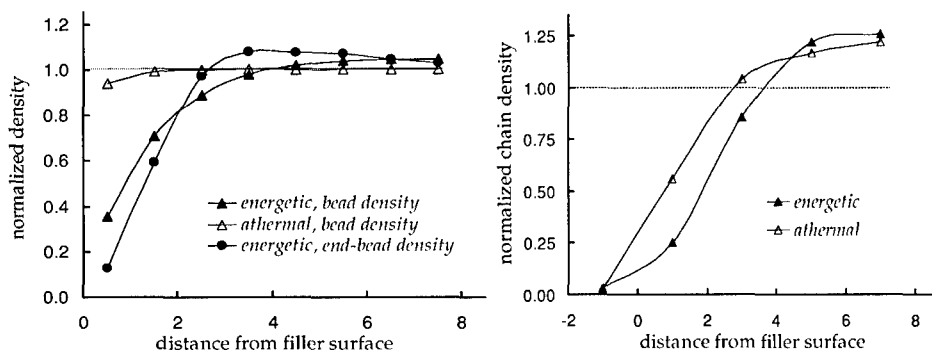


Figure 1. Bead (a) and chain (b) number density profile next to the spherical filler.

entropic force that retracts the chains from the wall (spherical or planar), and by the densification effect of the cohesive interactions in the bulk polymer (see the difference between the "energetic" and "athermal" curves). A small number of chains that wrap around the filler have their centers of mass within the particle (negative distance from filler surface).

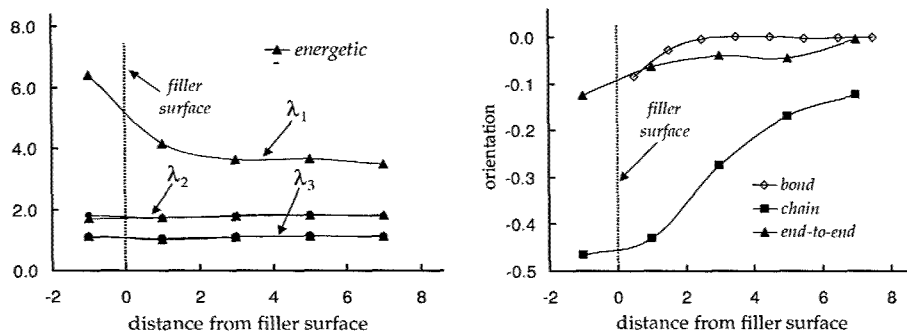
The chain size was determined by computing the gyration tensor for chains having their centers of mass at various distances from the filler surface. In the bulk, chains have an ellipsoidal shape, the semi-axes of the ellipsoid being given by the eigenvalues of the gyration tensor. The results obtained for the present system are shown in Fig. 2. The three semi-axes of magnitude in the bulk  $\lambda_1 = 3.89$ ,  $\lambda_2 = 1.84$  and  $\lambda_3 = 1.14$ , are shown in Fig. 2a. Interestingly, chains having their centers of mass in the first bin next to the wall have dimensions similar to those in the bulk. The few chains having their centers of mass within the filler are swollen.

The orientation of the long semi-axis of the ellipsoidal chains is random in the bulk. As the chain center of mass approaches the wall, the chains tend to align with their large semi-axis in the direction tangential to the interface (a "docking" transition previously observed next to a flat wall). Fig. 2b shows the second moment of the orientation distribution of the long semi-axis (labeled "chain"). Perfect orientation in the tangential direction corresponds to a value of  $-0.5$  of this measure. Preferential orientation is observed on all scales, from the bond to the chain scale. The orientation of bonds and chain end-to-end vectors is weaker than that of the coil (Fig. 2b).

Higher confinement induced by a further reduction of the wall-to-wall distance leads to a reduction of chain dimensions, with chains "docking" to the wall in all cases [3]. This result is in agreement with data published by Vacatello [4], but disagree with the model advanced by Mark and collaborators [5]. Our data are discussed against both sets of results in [3].

### Elastic moduli of the system of chains

The elasticity of the system of chains is derived here based on the free energy of the system. The total free energy,  $W$ , contains three energetic and an entropic term:  $W = U^{nb} + U^b + U^f - TS$ . The energetic terms are due to non-bonded interactions, between beads not directly connected along a chain, to bonded interactions, between directly connected beads, and to the energetic interaction between the filler and the matrix. The stiffness of the system of chains in the model



**Figure 2.** (a) Semi-axes of the ellipsoidal chains as a function of the position of their centers of mass with respect to the wall. (b) A measure of the preferential orientation of chains, bonds and chain end-to-end vector in the direction tangential to the spherical filler.

results as the second derivative of the free energy density ( $w = W/V$ ) with respect to the deformation gradient tensor  $\mathbf{F}$ ,  $C_{ijkl} = \partial^2 w / \partial F_{ij} \partial F_{kl}$ . Hence, the stiffness has 4 components corresponding to the respective terms in the free energy.

The total energy due to non-bonded interactions,  $U^{nb}$ , reads

$$U^{nb} = \int_{V_m} u^{nb} dV_m = \int_{V_m} \frac{1}{\Omega} \int_{V_r} n^{nb}(r_{RA}, \theta_{RA}, \phi_{RA}) \phi^{nb}(r_{RA}) dV_r dV_m, \quad (1)$$

where  $u^{nb}$  represents the non-bonded energy density, and  $V_m$  is the volume of the polymer matrix within the simulation cell. The non-bonded energy density may be expressed as the energy due to non-bonded interactions (cohesive energy) of a representative atom, RA, divided by the atomic volume  $\Omega$ . In the integral expression of this term,  $\phi^{nb}$  is the interatomic potential and  $n^{nb}$  stands for the density of non-bonded neighbors of the RA. The energy  $U^{nb}$  is estimated here within the local approximation. The inner integral in eqn. (1) is evaluated by neglecting the dependence of  $n^{nb}$  on  $(\theta_{RA}, \phi_{RA})$ , i.e. considering that an atom located in bin  $p$  has a neighborhood similar to that of an RA located in a homogeneous bulk of density  $\rho(r_p)$ , where  $r_p$  denotes the radial position of bin  $p$  with respect to the coordinate system centered at the center of the filler. The function  $\rho(r_p)$  is shown in Fig. 1a. For an atom located in a homogeneous material of uniform density  $\rho$ , the function  $n^{nb}$  may be expressed as  $n^{nb} = \rho g(r_{RA})$ , where  $g(r_{RA})$  is the pair distribution function of non-bonded neighbors about the RA. Then, the energy density due to non-bonded interactions in bin  $p$  may be written

$$u^{nb,p} = \frac{1}{\Omega} \frac{\rho_p}{\rho_{bulk}} \int_{V_r} \rho_{bulk} g(r_{RA}) \phi^{nb}(r_{RA}) dV_r = \frac{\rho_p}{\rho_{bulk}} u^{nb,bulk}. \quad (2)$$

Hence, the local stiffness in bin  $p$ , associated with non-bonded interactions, results from the stiffness of the bulk by scaling with the ratio of the local and bulk densities

$C_{ijkl}^{nb,p} = (\rho_p / \rho_{bulk}) C_{ijkl}^{nb,bulk}$ . Since the density varies with the distance from the wall, this relationship suggests that the matrix may be represented in the continuum sense by a material with graded elastic constants.

The contribution to stiffness of bonded interactions may be evaluated by a similar procedure. In the model considered here, the bonds are assumed to be rigid and hence,  $U^b = 0$ .

No energetic interactions between the filler and polymers are considered. Hence,  $U^b = 0$ . The more realistic case in which the polymers are attracted to the filler, while cohesive interactions are enabled in the bulk, is discussed in [6].

The entropic contribution to stiffness may be evaluated based on the classical formulation of stress production in polymeric systems and the entropic spring idea. The entropy of a chain is related to the probability distribution of the end-to-end vector,  $\mathbf{R}^{ee}$ . For Gaussian chains (an assumption shown to be valid in the system discussed here), the entropic contribution to the free energy per chain reads  $W = (3/2)kTR^{ee^2} / (C_{ee} b^2 N)$ . A deformation described by the deformation gradient tensor  $\mathbf{F}$  changes the end-to-vector from  $\mathbf{R}_0^{ee}$  in the undeformed configuration into  $\mathbf{R}^{ee} = \mathbf{F} \cdot \mathbf{R}_0^{ee}$ . Then, the contribution of a chain to the stiffness tensor becomes

$$C_{ijkl}^{entr} = \frac{\partial^2 w}{\partial F_{ij} \partial F_{kl}} = \frac{3}{2} \rho^c k T \frac{2\delta_{ik}}{C_\infty b^2 N} R_0^{\infty} R_{0L}^{\infty} \quad (3)$$

where  $\rho^c$  is the chain number density (given in Fig. 1b), and  $\delta_{ik}$  is the Kronecker delta. The total entropic contribution to the stiffness results by integrating over the whole chain orientation distribution. In the bulk, the chains are randomly oriented in space and the entropic contribution is given by  $C_{ijkl}^{entr} = \rho^c k T \delta_{ik} \delta_{jl}$ . In the neighborhood of the filler, the end-to-end chain vector is preferentially oriented in the direction tangential to the filler (Fig. 2b) which leads to an anisotropic  $C_{ijkl}^{entr}$ . As discussed in [6], the anisotropy is rather weak and hence is neglected in this analysis. It results that the entropic contribution to stiffness in bin  $p$  is proportional to the entropic contribution in the bulk, the proportionality factor being the ratio of the chain number density in bin  $p$  to that in the bulk,

$$C_{ijkl}^{entr,p} = (\rho_p^c / \rho_{bulk}^c) C_{ijkl}^{entr,bulk}.$$

Hence, the stiffness in bin  $p$  normalized by the bulk stiffness reads

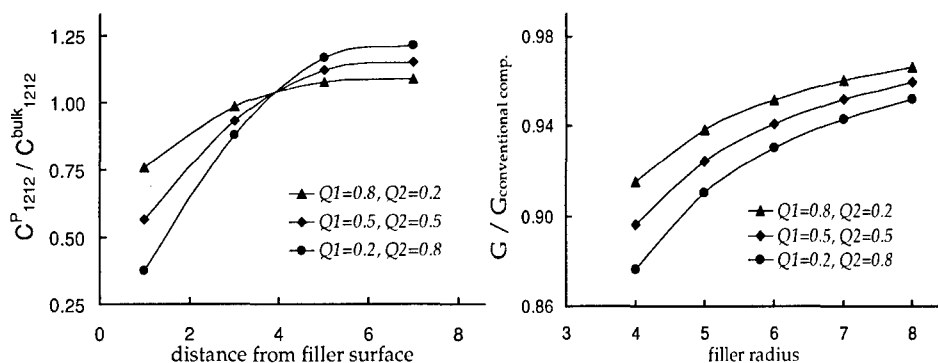
$$\frac{C_{ijkl}^p}{C_{ijkl}^{bulk}} = (\rho_p / \rho_{bulk}) Q_1 + (\rho_p^c / \rho_{bulk}^c) \delta_{ik} \delta_{jl} Q_2, \text{ where } Q_1 = C_{ijkl}^{nb,bulk} / C_{ijkl}^{bulk} \text{ and } Q_2 = C_{ijkl}^{entr,bulk} / C_{ijkl}^{bulk}.$$

The variation of the two density ratios with the distance from the wall is shown in Figs. 1a and b, while  $Q_1$  and  $Q_2$  are constants, independent of the distance to the wall. The two terms  $Q_1$  and  $Q_2$  represent the fraction of the total stiffness of the bulk due to energetic and entropic interactions, respectively. Their magnitude depends on temperature and bulk density. Here, we take these quantities as parameters (note that  $Q_1 + Q_2 = 1$ ). At low temperatures, the entropic component is small and the first term dominates. As the temperature increases, the second term becomes important. The stiffness gradient in the neighborhood of the filler corresponding to 3 pairs ( $Q_1, Q_2$ ) is shown in Fig. 3a.

Once the stiffness tensor is defined in each layer, homogenization theory may be used to evaluate the moduli of the composite. For this purpose, the multi-inclusion model proposed by Nemat-Nasser and Hori [7] was used. The expression for the overall composite stiffness tensor is given by  $\bar{C} = C^{bulk} [I + (S - I) \Phi^R] (I + S \Phi^R)^{-1}$ , where  $C^{bulk}$  is the stiffness tensor of the bulk,  $S(\Omega; C^{bulk})$  is Eshelby's tensor for a spherical inclusion  $\Omega$  embedded in a solid of stiffness  $C^{bulk}$ , and  $\Phi^R = \sum_{p=1}^n (f^p - f^{p-1}) \Psi^p(\Omega; C^{bulk}, C^p)$ ,  $\Psi^p = -[S(\Omega; C^{bulk}) + (C^p - C^{bulk})^{-1} C^{bulk}]^{-1}$  [7].

### Filler size effect

Decreasing the size of the filler ( $R$ ) at constant volume fraction requires a proportional reduction of the cell size and of the wall-to-wall distance between fillers. In this process, the thickness of the graded layer, which is essentially a function of the chain length  $N$ , does not scale. Hence, the volume fraction occupied by the graded material increases and a size effect in the overall composite moduli is evidenced. The bulk and shear moduli of the composite are evaluated for the system with 6.5% filler volume fraction. The result for the shear modulus is shown in Fig. 3b for three ( $Q_1, Q_2$ ) pairs. The composite modulus is normalized by the modulus of the corresponding conventional composite, with no graded region, and having the same filler volume fraction. In the limit of large fillers, the modulus tends to that of the conventional composite (to 1 in Fig. 3b). As the minimum wall-to-wall distance between fillers becomes



**Figure 3.** (a) Variation of matrix shear modulus with the distance from the wall. The variation is mainly due to reduced bead and chain number density at the wall. (b) Scaling of the composite shear modulus with the size of the filler ( $R$ ) at constant filler volume fraction (6.5%).

smaller than about  $5R_g$ , the modulus departs from that of the conventional composite exhibiting a sensible size effect. The minimum filler separation considered was about  $2R_g$  (which corresponds to  $R = 4$ ) in order for the graded regions of neighboring fillers not to overlap. The shear modulus decreases as the filler size is reduced. The bulk modulus has a similar variation.

## CONCLUSIONS

The structure of the polymer matrix in the close neighborhood of a spherical nanofiller in polymer-based nanocomposites is studied. It is shown that the chains having their center of mass close to the filler, rotate without deforming with their large semiaxis in the direction tangential to the filler. The chain number density is reduced at the wall. The stiffness tensor of this graded material was derived based on the free energy of the system which, in turn, was evaluated based on the atomic and molecular structure. The composite was represented by a multi-phase continuum model and homogenized using the homogenization theory. The effect on the overall composite moduli of reducing the filler size at constant filler volume fraction was evaluated.

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